

PTO 08-4066

CC=JP DATE=19841026 KIND=A  
PN=59189103

WATER-ABSORBING AGENT  
[Kyushuzai]

Tsuneo Tsubakimoto, et al.

UNITED STATES PATENT AND TRADEMARK OFFICE  
Washington, D.C. April 2008

Translated by: FLS, Inc.

PUBLICATION COUNTRY	(19):	JP
DOCUMENT NUMBER	(11):	84189103
DOCUMENT KIND	(12):	A
PUBLICATION DATE	(43):	19841026
APPLICATION NUMBER	(21):	S58 [1983]-62264
DATE OF FILING	(22):	19830411
ADDITION TO	(61):	
INTERNATIONAL CLASSIFICATION	(51):	C 08 F 8/14; A 61 L 15/00; C 08 F 8/30, 20/06
PRIORITY	(30):	
INVENTORS	(72):	MIMOMURA Tadao; IRIE Yoshio
APPLICANT	(71):	Nippon Shokubai Kagaku Kogyo Co., Ltd.
DESIGNATED CONTRACTING STATES	(81):	
TITLE	(54):	Water-Absorbing Agent
FOREIGN TITLE	[54A]:	Kysuizai

## 1. Title of the Invention

Water-Absorbing Agent

## 2. Scope of the Claims

1. A water-absorbing agent obtained by mixing one or more crosslinking agents selected from the group consisting of polyglycidyl ether compounds, polyaziridine compounds, polyamines and polyisocyanate compounds with a carboxyl group-containing water-absorbing resin powder at a ratio ranging from 0.001 to 10 parts by weight relative to 100 parts by weight of the water-absorbing resin powder, if desirable, by performing a heat treatment such that the water-absorbing resin powder and the crosslinking agent react with each other to carry out crosslinking of the molecular chains at least near the surface of the water-absorbing resin powder.

2. The water-absorbing agent as described in Claim 1, wherein the carboxyl group-containing water-absorbing resin is a polymer of the acrylic acid alkali metal salts obtained by forming a gel-form hydrated polymer by copolymerization of a monomer component consisting of 100 parts by weight of an acrylate monomer comprising 1 to 50 mol% of acrylic acid and 50 to 99 mol% of an acrylic acid alkali metal salt, and 0 to 5 parts by weight of a crosslinking monomer in an amount of 20 wt% or more, subsequently followed by thermal drying.

3. The water-absorbing agent as described in Claim 1, wherein the water-absorbing resin powder contains a powder that passes through 60

---

\* Numbers in the margin indicate pagination in the foreign text.

mesh at 70 wt% or greater

### 3. Detailed Description of the Invention

The present invention relates to a water-absorbing agent. More precisely, it relates to a water-absorbing agent that absorbs an aqueous material to a higher degree when brought into contact with an aqueous material and that has a high water retention ability even under pressure.

Conventionally, attempts have been made to use a water-absorbing resin as one constituent material in menstrual diapers, disposable diapers or hygienic material absorbing other body fluids.

For example, the following water-absorbing resins are known: hydrolysate of starch-acrylonitrile graft polymers, neutralized product of starch-acrylic acid graft polymers, saponified product of vinyl acetate-acrylic acid ester copolymers, hydrolysate of acrylonitrile copolymers or acrylamide copolymer or their crosslinked product, auto-crosslinking type sodium polyacrylate obtained by reverse phase suspension polymerization and polyacrylic acid neutral crosslinked materials.

However, these prior water-absorbing resins have the fatal /14  
drawback that the absorption rate is slow when compared to cotton pulps and paper. For this reason, the present status is that when the prior water-absorbing resin is incorporated in a disposable diaper, after urine has been discharged, the skin is in contact with urine for a while due to the slow rate of water absorption, giving the person a feeling of discomfort so that it takes a little while for

the user to achieve a dried state. Thus, many attempts have been made.

For example, in order to enlarge the surface area, the particle sizes are reduced, granules are produced or a scaly surface is attempted.

In general when the particle sizes of the water-absorbing resin are reduced, a phenomenon of so-called "insoluble mass" occurs when it is exposed to urine, which delays the absorption speed. If a water-absorbing resin is formed in a granular form, each granule becomes an "insoluble mass" so that a phenomenon of delaying the absorption rate is detected. If a water absorption resin is formed in a scaly form, the absorption rate is improved considerably, but it is still inadequate. In addition, there are restrictions from the aspect of processes to produce a product in a scaly manner so that the drawback is that the equilibrium moisture absorption is low. Further, in the case of a scaly product, the product inevitably becomes very bulky so that a large system is required for transportation and storage, which implies that the system is not economical.

The inventors earnestly investigated in an attempt to solve the aforementioned problem with the conventionally known water-absorbing resins and discovered the following fact. A water-absorbing agent is obtained by mixing one or more crosslinking agents selected from the group consisting of polyglycidyl ether compounds, polyaziridine compounds, polyamines and polyisocyanate compounds with a carboxyl group-containing water-absorbing resin powder and, if desirable, a

heat treatment wherein the water-absorbing resin powder and the crosslinking agent are reacted to cause crosslinking of the molecular chains at least near the surface of the water-absorbing resin powder. As a result, we achieved the present invention.

Thus, the object of the present invention is to provide a water-absorbing agent having a high absorption rate and also having a large equilibrium moisture absorption.

Namely, the water-absorbing agent of the present invention is obtained by mixing one or two or more crosslinking agents selected from the group consisting of polyglycidyl ether compounds, polyaziridine compounds, polyamines and polyisocyanate compounds with a carboxyl group-containing water-absorbing resin powder at a ratio ranging from 0.001 to 10 parts by weight relative to 100 parts by weight of the water-absorbing resin powder, if desirable, by performing a heat treatment such that the water-absorbing resin powder and the crosslinking agent are reacted with each other to carry out crosslinking of the molecular chains at least near the surface of the water-absorbing resin powder.

It is important that the water-absorbing resin used in the present invention contains a carboxyl group. One or more compounds selected from the group consisting of hydrolysates of starch-acrylonitrile graft polymers, partial neutralization products of starch-acrylonitrile graft polymers, saponified products of vinyl acetate-acrylic acid ester copolymers, hydrolysates of acrylonitrile copolymers or acrylamide copolymers or their crosslinked products,

partially neutralized polyacrylic acid and partially neutralized crosslinked products of polyacrylic acid can be used as a water-absorbing resin. Further, it is desirable to have a crosslinked structure. However, those having no crosslinked structure can also be used.

Among these water-absorbing resins, the water-absorbing resins shown in each of the following paragraphs (1) through (5) can be listed as those that are used favorably in the present invention:

- (1) Polymers of acrylic acid alkali metal salts obtained by forming a gel-form hydrated polymer by copolymerization of a monomer component comprising 100 parts by weight of an acrylate monomer consisting of 1 to 50 mol% of acrylic acid and 50 to 99 mol% of alkali metal acrylates with 0 to 5 parts by weight of a cross-linked monomer in an amount of 20 wt% or more in an aqueous solution copolymerization, followed by subsequent heating and drying.
- (2) Water-absorbing resins obtained by dispersion suspension polymerization of an aqueous radical polymerization initiator in an alicyclic and/or aliphatic hydrocarbon solvent, if desirable, and an aqueous solution of acrylic acid containing a crosslinked monomer and/or an alkali metal salts acrylate in the presence of a surfactant with HLB of 3 to 12.
- (3) Saponified products of copolymers of vinyl ester and ethylene unsaturated carboxylic acid or their derivatives.
- (4) Water-absorbing resins obtained by polymerizing a monomer

/15

having starch and/or cellulose, carboxyl group or a monomer producing a carboxyl group by hydrolysis, if desirable, with a crosslinked monomer in an aqueous medium, if desirable, followed by additional hydrolysis.

- (5) Water-absorbing resins obtained by reacting an alkali material with an anhydrous maleic acid copolymer consisting of at least one or more monomer selected from the group consisting of  $\alpha$ -olefins and vinyl compounds with anhydrous maleic acid and, if desirable, by reacting a polyepoxy compound with the above-mentioned reaction product.

With respect to the amount of carboxyl groups present in the water-absorbing resins, there are no particular limitations as long as a carboxyl group is present. A desirable amount is 0.01 equivalents of the carboxyl group per 100 g of the water-absorbing resin. For example, in the case of partially neutralized products of polyacrylic acid, a non-neutralized portion is preferably present at a ratio of 1 to 50 mol%.

The shape of the powder of the water-absorbing resins used in the present invention can be spherical obtained by reverse phase suspension polymerization, scaly shape obtained by drum drying; or amorphous shape obtained by pulverizing the resin blocks. In terms of the water-absorbing resin powder particle size, a smaller size is preferred from the standpoint of absorption speed, which is that the ratio of those passing through 60 mesh is 70 wt% or greater is desirable. If the ratio of those passing through 60 mesh is 70 wt% or



less, the absorption speed tends to decrease. A crosslinking agent to be used in the present invention has two or more functional groups per molecule that can react with a carboxyl group. One or more compounds can be selected from the group consisting of polyglycidyl ether compounds, polyaziridine compounds, polyamine compounds and polyisocyanate compounds.

As polyglycidyl ether compounds, ethylene glycol glycidyl ether, glycerin glycidyl ether and the like can be listed.

As polyaziridine compounds, "Chemitite PZ-33" (2,2-bishydroxymethylbutanol-tris[3-(1-aziridinyl)propionate]), "Chemitite HZ-22" (1, 6-hexamethylene diethyleneurea), "Chemitite DZ-22" (diphenylmethane -bis-4, 4'-N, N'diethylene urea) (all of the above are products by Nippon Shokubai Kagaku Kogyo Co., Ltd.) and the like can be listed. As polyamine compounds, ethylenediamide, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, pentaethylenehexamine, polyethyleneimine and the like can be listed. As polyisocyanate compounds, 2,4-trilene diisocyanate, hexamethylene diisocyanate and the like can be listed.

In addition, these compounds can be used alone or in a combination of two or more kinds. The amount of a crosslinking agent to be used in the present invention depends upon the kind of the water-absorbing agent. Generally, a desirable ratio ranges from 0.001 to 10 parts by weight relative to 100 parts by weight of the water-absorbing resin. If it exceeds 10 parts by weight, the crosslinking density becomes too high, resulting in a reduced multiplication of

water absorption. In contrast, if the amount is less than 0.001 parts by weight, there is no effect of the use of a crosslinking agent.

In the present invention, an ordinary mixing agent can be used while mixing a water-absorbing resin powder with a crosslinking agent. For example, a V type mixer, a ribbon type mixer, a screw type mixer, a rotary disk type mixer, a gas flow type mixer and the like can be used.

The reaction between the carboxyl group of the water-absorbing resin powder and a crosslinking agent, as in the case when using an aziridine compound as a crosslinking agent, can be carried out at room temperature. However, in order to accelerate the reaction, it is generally desirable to perform a heat treatment. The heat treatment temperature depends upon the crosslinking agents, a desirable temperature range is as follows: typically 50 to 300°C and preferably 90 to 250°C in the case of polyglycidyl ether compounds; typically 10 to 300°C and preferably 20 to 250°C in the case of polyaziridine compounds; typically 90 to 300°C and preferably 120 to 150°C in the case of polyamine compounds; and typically 10 to 300°C, preferably 20 to 250°C, in the case of polyisocyanate compounds.

For the heat treatment of the water-absorbing resin powder and the crosslinking agent mixture, generally a dryer or heating furnace can be used. For example, a groove type agitator dryer, rotary dryer, disk dryer, blender dryer, fluid bed dryer, gas flow dryer, IR-ray dryer and the like can be used.

When mixing and carrying out a heat treatment, if heating is /16 possible in the mixer, both blending and heat treatment can be executed simultaneously in the mixer. If the heat treatment device can be stirred, a heat treatment can be carried out simultaneously while mixing in the heat treatment device.

The water-absorbing agent of the present invention demonstrates superior performance compared to the prior water-absorbing agents. That is, the water-absorbing agents of the present invention can be obtained by an industrially simple method such as mixing and reacting a water-absorbing resin with a crosslinking agent. Unlike the prior water-absorbing resins, the "insoluble mass" phenomenon may not occur easily so that a high absorbing rate can be achieved. In addition, the unexpected effect of the powder caking in a low moisture state can be prevented.

The water-absorbing agents of the present invention can be used as an absorbing agent to be used in disposable diapers and menstrual pads as well as a wide range of usages including coagulation of sludge, prevention of condensation on building materials, water retaining agents or dryers for gardening.

The present invention will be described in detail below with reference to the following embodiments, but not limited by these embodiment. Unless otherwise specifically mentioned, "%" shown in these embodiments indicates "wt%" and "parts" indicates "parts by weight".

#### Embodiment 1

A 43% aqueous solution (4000 parts) of an acrylate monomer consisting of sodium acrylate 74.95 mol%, acrylic acid 25 mol% and trimethylolpropane triacrylate 0.05 mol% was stationary polymerized at 55 to 80°C under a nitrogen gas atmosphere using ammonium persulfate 0.6 parts and sodium hydrogen sulfite 0.2 parts to obtain a gel-form hydrate polymer. After drying this gel-form hydrate polymer in a hot air dryer at 180°C, the dried matter was pulverized using a shaking type pulverizer to separate a portion passing through 60 mesh (powder (A)).

Ethylene glycol diglycidyl ether 0.5 parts was added to the powder (A) and blended with a ribbon blender. A heat treatment was applied for 30 minutes by raising the hot medium temperature in the jacket of ribbon blender to 180°C. The temperature of the material at the end of the heat treatment was 171°C.

The water-absorbing agent (1) 0.2 g obtained above was packed uniformly in an unwoven fabric tea bag-shaped bag (40 mm x 150 mm) which was then dipped into 0.9% saline water. The weight was measured at 30 seconds after and 10 min. after. A tea bag alone was used as a blank of the absorption weight. The degree of absorption of the water-absorbing agent was calculated using the following formula.

$$\text{Absorption magnification} = \frac{\{\text{Weight after absorption (g)} - \text{blank (g)}\}}{\text{weight of the powder (g)}}$$

Further, the presence/absence of "insoluble mass" generation was determined by dropping a small quantity of the water-absorbing agent

on a paper moistened with water and the behavior was observed.

Table 1 shows the results. When compared to powder (A), the water-absorbing agent (1) did not generate "insoluble mass", indicating that the absorption rate was improved significantly.

#### Embodiment 2

The powder (A) obtained in Embodiment 1 (100 parts) and triethylene tetramine (1 part) were blended in a kneader. This blend was continuously supplied and discharged into/from a puddle dryer (Nara Kikai Seisakusho K.K.) to carry out a heat treatment. At this time, the mean retention time was 20 min. Further, the material temperature at the discharge outlet was 190°C.

The water-absorbing agent (2) obtained was evaluated as in Embodiment 1. The results are shown in Table 1.

#### Embodiment 3

The powder (A) obtained in Embodiment 1 (100 parts) and "Chemitite PZ-33" (Nippon Shokubai Kagaku Kogyo Co., Ltd., 2,2-bishydroxymethylbutanol-tris [3-(1-aziridinyl)propionate]) (0.5 parts) were blended with a ribbon blender and the blend was left standing for 3 days at room temperature (20-30°C) to carry out the reaction. A water-absorbing agent (3) was obtained.

The water-absorbing agent (3) obtained was evaluated as in Embodiment 1. The results are shown in Table 1.

#### Embodiment 4

The powder (A) obtained in Embodiment 1 (100 parts) and 2,4-tolylene diisocyanate (1 part) were blended with a Nauta mixer

(Hosokawa Micron Co., Ltd.) and a heat treatment was performed in a disk type dryer. The material temperature at the discharge outlet was 100°C.

The water-absorbing agent (4) obtained was evaluated as in /17  
Embodiment 1. The results are shown in Table 1.

#### Embodiment 5

Corn starch (50 parts), water (200 parts) and methanol (1000 parts) were placed in a reactor equipped with a stirrer, a nitrogen blowing tube and a thermometer and the mixture was stirred under nitrogen gas flow at 50°C for 1 hour and then cooled to 30°C. Acrylic acid (25 parts), sodium acrylate (76 parts), methylene bis(acrylamide) (0.5 parts), ammonium persulfate (0.1 parts) as a polymerization catalyst and sodium hydrogen sulfite (0.1 parts) as an accelerator were added and the reaction was carried out at 60°C for 4 hours. As a result, a white suspension was obtained.

A powder obtained by filtration of the white suspension was rinsed with a mixture of water and methanol (water : methanol ratio by weight 2 : 10) and dried at 60°C under reduced pressure for 3 hours. The dry powder was crushed and separated through a 60-mesh wire sieve and a 60 mesh passing portion (powder (B)) was obtained. Ethylene glycol glycidyl ether (1 part) was added to 100 parts of the powder (B) and the mixture was blended with a rotary disk type blender. The mixture obtained was treated by a heat treatment by blowing hot air at 170°C for 10 minutes to obtain a water-absorbing agent (5). The material temperature at the discharge was 165°C. The water-absorbing

agent obtained was evaluated as in Embodiment 1. The results are shown in Table 1.

#### Embodiment 6

Benzoyl peroxide (0.5 parts) was added as a polymerization initiator to a mixture consisting of 60 parts of vinyl acetate and 40 parts of methyl methacrylate and the mixture was dispersed in water (300 parts) containing 3 parts of partially saponified polyvinyl alcohol and 10 parts of salt. The suspension polymerization was carried out at 65°C for 6 hours. The mixture was filtered and dried to obtain a copolymer. The copolymer obtained was saponified, washed and dried. The dried copolymer was crushed and classified by passing particles through a 60 mesh sieve. A powder passed through a 60 mesh was called powder (C).

Triethylene tetramine (1 part) was added to 100 parts of the powder (C) and the mixture was placed in a ribbon blender whose jacket was heated to 230°C with a hot medium. While blending the mixture for 15 min. a heat treatment was applied to obtain a water-absorbing agent (6). The material temperature at the discharge was 185°C. The water-absorbing agent (6) was evaluated as in Embodiment 1. The results are shown in Table 1.

#### Embodiment 7

300 parts of n-hexane was placed in a reactor where 0.7 parts of sorbitan monostearate was dissolved. Subsequently, 30 parts of acrylic acid was dissolved in 40 parts of water and then neutralized with 12.5 parts of caustic soda and additionally, 0.05 parts of

potassium persulfate was dissolved. This monomer solution was added and dispersed. While maintaining the system under nitrogen gas at 65°C, the polymerization was carried out for 5 hours. At the end of polymerization, the product was dried in a vacuum to obtain a powder (D).

One part of glycerin diglycidyl ether was added to 100 parts of the powder (D) and blended with a V type mixer. The mixture obtained was thinly spread on top of a belt conveyor which was passed through an IR dryer to carry out a heat treatment. As a result, a water-absorbing agent (E) was obtained. An average heating time was 4 minutes and the material temperature at the dryer exit was 190°C.

The water-absorbing agent (7) was evaluated as in Embodiment 1. The results are shown in Table 1.

#### Embodiment 8

Isobutylene-maleic anhydride copolymer (154 parts), caustic soda (64 parts) and water (398 parts) were mixed and the mixture was heated at 90°C for 2 hours while stirring to obtain a homogeneous aqueous solution. Subsequently, 2.5 parts of glycerin diglycidyl ether was added to the aqueous solution and after blending, the mixture was poured into a vat. The crosslinking reaction was carried out in a hot air dryer at 110°C. After drying, the powder was classified and a 60 mesh pass portion was separated as a powder (E).

Chemitite PZ-33 (0.5 parts) was added to 100 parts of the powder (E) and blended with a ribbon blender. The mixture was placed at a thickness of 5 mm on top of a stainless steel dish and the dish was



left in a thermostatic chamber at 50°C for one day to obtain a water-absorbing agent (8).

The water-absorbing agent (8) was evaluated as in Embodiment 1.

The results are shown in Table 1.

/18

Table 1

		Degree of absorption		Presence/absence of "insoluble mass" generation (note)
		After 30 seconds	After 10 minutes	
Embodiment 1	Powder (A)	31	62	X
	Water-absorbing agent (1)	52	72	⊙
Embodiment 2	Water-absorbing agent (2)	53	71	⊙
Embodiment 3	Water-absorbing agent (3)	52	69	⊙
Embodiment 4	Water-absorbing agent (4)	51	69	⊙
Embodiment 5	Powder (B)	25	35	X
	Water-absorbing agent (5)	38	42	⊙
Embodiment 6	Powder (C)	28	48	X
	Water-absorbing agent (6)	40	49	⊙
Embodiment 7	Powder (D)	25	38	X
	Water-absorbing agent (7)	44	55	⊙
Embodiment 8	Powder (E)	23	33	X
	Water-absorbing agent (8)	40	50	⊙

(Note) ⊙: "insoluble mass" not found.

X: "insoluble mass" appeared.

As clearly shown in Table 1, the water-absorbing agent of the present invention did not cause a phenomenon of "insoluble mass" and a high absorption speed was maintained.